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A STUDY OF THE PREPARATION AND ELECTRICAL PROPERTIES OF CERTAIN CLAY FILM DIELECTRICS

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STATEMENT OF THE PROBLEM

An experimental study was made of bentonite clay films (alsifilms) with respect to their physical, (4, 5, 6, 7, 8), electrical and colloidal properties. The variables considered were: bentonites from various sources, bentonites of various capacities for base exchange, bentonites of various particle size distributions, various base exchange agents, and subsequent heat cures or pressure and heat cures on the base exchanged films.

CHOICE OF CLAY

The choice of the clay to be used in this study proved to be very important because of the differences in the range of particle sizes of samples from various sources. To make a successful alsifilm there had to be no clay particles greater in size than five microns and most had to be less than that size. Some clays occur naturally with larger proportions of these small particles than do others. Bentonites are favorable in this respect in contrast to halloysite, for example, which has too small a percentage of the particles in the desired size range. Not all bentonites have the same range of particle sizes, however, as is shown in Table I.

Another basis of comparison and contrast of these various clays, in addition to particle size, is the chemical composition. Not much correlation has been drawn between chemical composition and film properties other than the color of the film. All films prepared in this study had a light tan color before base exchange and heat cure. This color was attributed to the presence of iron oxides in the bentonite. This belief was later substantiated

TABLE I

Type of Clay	Percentages of Various Particle Sizes: Larger than 74 micron	Larger than 44 micron	Less than 44 micron	1 - 44 micron	Less than 5 micron	3-5 micron	0.5-5 Micron	0.5-1 micron	Less than 0.5 micron
Volclay (1)		0.1-4		2-3	94			4-5	80-90
Average Colloidal Bentonite (1)		3-4		5-10				20-30	60-70
Non-bentonite plastic clay (1)		15-20		30-50				25-40	15-35
Fisher (B-237/2) (3)			95						
Bennett Clay (15)	3-4								
Panther Creek (1)					70		35		35
Wyodak micro-mesh (17)						99			

Attaclay (2) Average particle size by air permeation method is 1-2 microns

Please Note: 1 micron is approximately 1/25000 inch; 50 microns diameter--smallest single particle visible to the human eye

in part by the light colored clay obtained from the base exchange experiments when iron was replaced by hydrogen. From the point of view of low iron content, Bennett clay (Table II) seemed ideal. However, the average particle size of this clay was entirely too large to permit the preparation of suspensions which could be centrifuged. Most of the clay settled out in the 24 hour period before the actual centrifuging was begun. Table II gives the approximate composition of a number of the bentonite clays.

The final selection of clay used in this work was Wyodak micro-mesh and American Colloid Volclay. In preliminary work, a bentonite (B-237/2) furnished by Fisher Scientific Company was used.

CENTRIFUGING

A fractionation of the clay in water suspension was necessary in order to concentrate the particles in the desired size range from the colloidal clays selected. This operation was carried out with a Sharples Super Centrifuge (Type M-41-24). Various slip feeds and RPM's of the bowl were tried before the best procedure was found.

In the first separations of Fisher Scientific bentonite, the solid material left in the centrifuge bowl after the second pass was suspended again in distilled water, boiled to the gel stage, and laid down in the film forming step. In this procedure the slip feed of the first pass was 90 ml. per minute at a bowl speed of 12,000 RPM. For the second pass the slip feed was 20 ml. per minute and the bowl speed was 16,000 RPM. Although a large percentage of the particles was in the size range less than 0.07 micron in diameter, enough of the particles were greater than that size to give a very course and brittle film.

TABLE II

CHEMICAL ANALYSIS OF VARIOUS CLAYS

Chemical Analysis Percent	Volclay (1)	Panther Creek Bentonite (1)	Argosite (15)	Bennett Clay (15)	Wyodek micro-mesh (17)	Fisher (3)	Attapulgus Clay (2)
SiO_2	64.32	64.17	60.16	71.00	65.17	63.20	68.43
Al_2O_3	20.74	17.14	19.88	13.00	16.64	20.54	12.56
Fe_2O_3	3.03	4.81	2.97	0.85	4.91	3.25	4.94
FeO	0.46		0.54			0.26	
CaO	0.52	1.48	0.67	1.20	1.39	1.30	1.67
MgO	2.30	3.90	2.20	2.04	3.78	2.49	9.82
Na_2O	2.59	0.21	2.60	2.30	0.19	2.16	0.25
K_2O	0.39	0.48	0.40	0.60	0.46	0.50	0.70
Essential Moisture	5.14		4.91			5.06	
Ignition Loss		7.78	5.58	9.13	7.44	7.19	12.10
pH (H_2O suspension)	8.5-9.5	6-6.5	9.2	5.1			7-7.6

Further refinements in the centrifuging procedure were made. Four or six passes were run on an original two percent suspension of the bentonite in distilled water. The suspension stood for 24 hours after its preparation before the centrifuging began. The colloidal gel was made from the liquid pass of the last separation and not from the larger particles in the bowl. Both the Wyodak and the American Colloid clays were treated in this way.

Hauser and Reed (14) have worked out a graphical method for correlating the RPM and the slip feed of a Sharples Super Centrifuge with the particle sizes settled out under these conditions. These particle sizes along with the bowl speeds and slip feeds employed in the four and the six step procedures are given in Tables III and IV.

TABLE III

FOUR STEP CENTRIFUGING PROCEDURE WAS AS FOLLOWS:

Bowl Speed (RPM)	Slip Feed (ml. per minute)	Particle size in the pass
6000	100	Less than 0.4 micron
10000, later 8000	70, later 90	0.2 micron, later 0.3 micron
10000	70	0.2 micron and less
10000	70	0.2 micron and less

Substantial evaporation of the last pass in the four step procedure listed in Table III gave a gel which resulted in a very thin film (0.001 inch in thickness) of fair strength. The smaller colloidal particles in the last pass of the six step procedure gave even a tougher film. The degree of texture smoothness and strength of the film was in indirect ratio to the size of the colloidal particles employed.

TABLE IV

SIX STEP CENTRIFUGING PROCEDURE WAS AS FOLLOWS:

Bowl Speed (RPM)	Slip Feed (ml. per minute)	Particle size in the pass
6000	100	Less than 0.4 micron
8000	90	0.3 micron and less
10000	70	0.2 micron and less
15000	40	0.1 micron and less
23000	40	Less than 0.07 micron
23000	40	Less than 0.07 micron

This method of using the liquid pass from the last run instead of the larger solid particles from the bowl in preparing the gel was in direct contrast to the methods of Hauser (5) and was similar to the method used by Aircraft-Marine Products Inc. (16)

EVAPORATION AND GEL FORMATION

Portions of the last pass from the centrifuging process were put into two liter beakers and evaporated on electric hot plates with constant mechanical stirring. Concentration continued in each case until the system had a viscosity very similar to that of a bentonite dispersion in water which, when tested by a Stormer Viscosimeter with a 99.26 gram weight attached, required 22.75 seconds for 100 revolutions at 30 degrees Centrigrade. A suspension of this viscosity gave a good gel.

Although the phenomenon of gelation is fairly common, it is still not thoroughly understood. Hauser and LeBeau (9) were able to prepare gels at concentrations of disperse phase as low as 0.05 percent. No alignment or grouping of the disperse phase was observed. It does not appear that an interlocking of long chain molecules need occur in order for gelation to take place.

FILM FORMATION

Various techniques have been employed in this operation. D. W. Light (10) added a resin to a colloidal clay suspension. The mixed suspension was evaporated from an amalgam surface. The plasticizer was burned out with oxygen.

Marshall (11, 12) formed films from electrodialyzed suspensions by evaporating them from copper or celluloid surfaces.

In this study many surfaces were tried for the evaporation step. Among others the gelatinous clay was spread on tin, copper, paraffin covered glass and aluminum surfaces. The films stuck to the tin, copper and aluminum surfaces and the paraffin coating on glass melted at the temperature necessary for an advanced rate of drying.

A very satisfactory wax coated glass surface was developed at the suggestion of Mr. F. A. Wells. (16) Johnson's "Paste Wax" was first dissolved in benzene (10 to 15 percent solution by weight) and the solution was sprayed on the glass surface in three or four successive applications. The solvent evaporated leaving only the thin wax coating which did not melt at temperatures of 50 degrees Centigrade. A deep scoring or scratch was placed as border around the glass surface area. This scoring served to hold the film in place at the edges later during the drying operation and to prevent premature peeling of the film from the surface.

The freshly boiled gel suspension, while still warm (50 to 60 degrees Centigrade), was poured on the wax coated surfaces (four by six inches) and was spread by a stainless steel scraping bar to exactly 0.075 inch thickness. It was pointed out by Mr. Wells (16) that initial wet layers much in excess of 0.075 inch thickness will not dry to tough self supporting films. They generally crack into many pieces, are not

self-supporting and are very brittle.

The next step, the drying of the film, was a critical one. Air drying at room temperature was first tried, but that procedure, requiring about a week, was too time consuming. Next, infra-red heating either from the top or the bottom was tried, but in every instance extreme cracking of the film occurred near the end of the operation and the film would stick to the glass surface. Finally, a forced air drying cabinet was built and drying in a stream of dust free air at 50 degrees Centigrade for about four hours gave the desired results. If the film was left in the cabinet for longer periods, however, it would weld to the glass surface and be impossible to remove in one piece. In the drying procedure the gel layer shrank to 1/75 th of its original wet thickness, but no cracking or surface separation was noted. Thicker films could best be prepared by laminating a number of these thin dry films under treatment of heat and pressure.

Some work was also done on self-supporting clay films reinforced with asbestos fibers and cellulose shreds. One to two percent by weight of shredded asbestos or filter paper was stirred vigorously into the gelation mixture of the clay. The rest of the procedure of film forming and drying was carried out as above. These films were tough but were not uniform in texture. This approach was abandoned when strong self-supporting films containing only bentonite were prepared.

BASE EXCHANGE

A clay is really a very complex anion associated with several cations. In aqueous suspension these cations dissociate and the clay micelle may be thought of as a dissociated electrolyte. One cation of the clay may then be exchanged for another just as a sodium soap will exchange its cation for calcium in hard water.

Not all clays will base exchange to the same extent. Also, after some cations are replaced by others, such as calcium for sodium, the clay greatly loses its swelling properties in water. It has been established that the order of preference of the clay anion for various cations is calcium, magnesium, potassium, hydrogen, sodium, lithium.(1)

It was hoped that the larger cations, approximating in size the dimensions between atoms in the montmorillonite minerals, would enter these spaces in the base exchange and be locked into them during the curing process. From this viewpoint larger cations would be preferred to smaller ones in the base exchange step. Large organic radicals were also of interest in base exchange work, but they would not withstand the heat cure process which appears to be necessary for reducing the power factor in these dielectric films to a desirable value.

Table V gives data on the exchangeable metallic bases in milli-equivalents per 100 grams of some clays. (1)

TABLE V

Cations	Bentonites: Volclay Wyoming	Bentonites: Panther Creek Mississippi	Bentonites: Lovite Nevada	Other Clays: Ohio Plastic Fire Clay	Other Clays: Kentucky Ball Clay
calcium	22.0	64.7	51.5	5.2	7.1
sodium	85.5	0.4	33.6	0.4	0.3
potassium	5.0	2.8	1.1	0.5	0.4
magnesium	1.0	1.0	19.1	1.3	3.8

Various base exchange techniques for bentonite were investigated using saturated barium chloride solutions with the clay. By one method the dried self-supporting transparent film was suspended in the saturated solution of the salt for a period of two or three hours. On removal of the film from solution, any crystals of the salt adhering to the film were washed off and the film was dried at 50 degrees Centigrade.

This procedure was generally unsatisfactory. In the base exchange process by this method the self-supporting film usually had a tendency to disintegrate. If the film was not destroyed in this manner in the base exchange step, then in the drying process in the forced air cabinet at 50 degrees Centigrade the film would curl and crack.

Successful base exchange reactions were carried out on the concentrated clay suspension from the sixth centrifuge pass in a Bradfield electrodialysis apparatus. Over a period of four hours the hydrogen clay formed in the central cell and the basic metal ions migrated to the cathode compartment. The voltage was 115 volts D. C., the amperage was 0.06, the rate of flow of distilled water through the anode compartment was 48 ml. per minute and through the cathode compartment was 30 ml. per minute. The acid clay was concentrated to a gel and a film was laid down. In order to introduce the desired cation into the clay, this film was treated with a saturated barium hydroxide solution while still attached to the wax coated glass plate. Another method was to add the barium hydroxide solution directly to the acid clay suspension, evaporate to the gel stage and then form the film. Either method worked satisfactorily. The only disadvantage was the small amount of acid clay that could be formed at any one time in the electrodialysis apparatus.

Another attempt was made to base exchange the cations before the film was poured. In this procedure dry Volclay was placed in a vertical glass column one inch in diameter and concentrated hydrochloric acid was poured through the packed column of clay. The acid flowed through extremely slowly under gravity. A definite displacement of ferric, calcium and magnesium ions from the clay by the hydrogen ion of the

acid was indicated by qualitative test run on the filtrate. The resulting hydrogen clay was washed and dried and was then used in making a two percent aqueous suspension in distilled water. This material was centrifuged six times by the regular procedure. The sixth pass did not yield a satisfactory gel when it was concentrated.

For some time base exchange of the hydrogen clay with the appropriate metal hydroxide seemed to be the ideal method of attack. It eliminated the need for removal of any foreign cations or anions since the hydrogen of the clay and the hydroxyl of the base gave only water which was lost in the drying step.

As suggested in work done by Hauser (6) barium chloride in various concentrations was thoroughly mixed with the concentrated gel. Films were then formed in the regular way. The mixture containing one percent barium chloride gave the best film of this type. The film was opaque and brittle. Films containing over one percent barium chloride added in this way were extremely brittle and contained crystals of barium chloride in the film surface. It does not appear that this process can be called base exchange, however, since no provision has been made in the procedure either for the removal of the cations (sodium, potassium, magnesium, calcium) naturally occurring in the clay or the anion (chloride, in this case) from the base exchange agent.

The most satisfactory way found in these studies to carry out the base exchange on a fairly large scale was to operate on the raw film after it had been dried in the cabinet and before it had been stripped from the glass plate on which it was formed. The plate with the film attached was immersed in a saturated solution of the barium

chloride for 15 minutes at room temperature. After this period of base exchange, the film, still attached to the plate, was rinsed with distilled water to remove any surface adsorbed crystals or foreign ions, dried and then stripped from the plate and cut into pieces for testing. The disadvantage of this method, of course, was that the exchange could take place from only one side of the film. The advantage was, however, that the film remained intact and flat in the saturated salt solution, a situation that did not exist when the detached self-supporting film was introduced directly into an aqueous solution.

Saturated solutions of the base exchange agents must be employed in order to prevent the peptization of the film when introduced into the aqueous solution.

Certain information concerning the base exchange agents used is given in Table VI.

CURING PROCESS

This treatment involved heat or heat and pressure applied to the film after the base exchange step. It was hoped that the cure would be an effective method of locking in the larger exchange cations between the atoms in the bentonite grouping of atoms. The process appeared necessary to lower the power factor to a desirable value in the completed film.

Curing treatments for varying lengths of time were employed using heat treatments up to 550 degrees Centigrade and heat and pressure treatments with a Carver electrically heated press up to 175 degrees Centigrade and 8.5 tons. These specific conditions are listed in Table VII.

The standard procedure which was finally adopted was a gradual heating from room temperature to 550 degrees Centigrade over a period

TABLE VI

COMPOUNDS USED IN SATURATED AQUEOUS SOLUTIONS IN THE BASE EXCHANGE STEP

Compound	Source	Grade	Code	Formula
cerium nitrate	Baker and Adamson	Puri-fied	1560	
cobalt chloride	J. T. Baker	C. P.		$CoCl_2 \cdot 6H_2O$
cadmium acetate	Baker and Adamson	Reagent	1481	$Cd(CH_3COO)_2 \cdot 2H_2O$
alum	.. .. ..	..	1238	$Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$
thorium nitrate	.. .. ..	..	2386	$Th(NO_3)_4 \cdot 4\ H_2O$
uranium acetate	.. .. ..	..	2404	$UO_2(CH_3COO)_2 \cdot 2H_2O$
chromium sulfate	Eimer and Amend	C. P.	C-338	$Cr_2(SO_4)_3 \cdot aq.$
sodium stannate	Baker and Adamson	Reagent	2292	$Na_2SnO_3 \cdot 3H_2O$
barium hydroxide	Merck	..	S-.7211	$Ba(OH)_2 \cdot 8H_2O$
lead acetate	Eimer and Amend	C. P.		$Pb(CH_3COO)_2 \cdot 3H_2O$
barium chloride	J. T. Baker	C. P.		$BaCl_2 \cdot 2H_2O$
calcium chloride	Eimer and Amend	C. P.	C-78	$CaCl_2 \cdot 6H_2O$
calcium hydroxide	.. .. ..	Reagent		$Ca(OH)_2$
mercurous nitrate	Baker and Adamson	..	1982	$Hg_2(NO_3)_2 \cdot 2H_2O$
mercuric nitrate	.. .. ..	..	1968	$Hg(NO_3)_2 \cdot H_2O$

CLAY FILM DIELECTRICS

TABLE VII

Sample Number	Clay Used	Remarks on Film Preparation	Base Exchange Agent
1	American Colloid Volclay	Clay suspension poured to 2 mm. thickness, then dried at 50 deg. C in a cabinet	Saturated $BaCl_2$ solution
2	..	.. ..	.. ..
3	..	.. ..	none
4	..	.. ..	Saturated $BaCl_2$ solution
5	..	.. ..	.. ..
6	..	.. ..	none
7	.	.. ..	Saturated $BaCl_2$ solution
8	Wyodak micro-mesh	.. ..	.. ..
11	..	.. ..	Saturated $CaCl_2$ solution
12	American Colloid Volclay	.. ..	.. ..
13	Wyodak micro-mesh	.. ..	none
14	American Colloid Volclay	.. ..	Saturated $Ba(OH)_2$ solution
17	Wyodak micro-mesh	.. ..	Saturated $Ca(OH)_2$ solution
19	..	.. ..	Saturated mercurous nitrate solution

Subsequent Treatment	Thickness (inches)	Dielectric Constant	Power Factor	Number
Heated at 560 C for 2 hours	0.005	6.98	11.1(percent)	1
Heated at 560 C for 14 hours	0.005	6.42	3.3	2
none	0.003	21.35	81.77	3
none	0.003	10.6	16.4	4
Heated at 175 C;10 min., 17000 lbs. pressure	0.0023	9.4	12.9	5
.. .. ..	0.0015	4.82	5.6	6
Heated at 175 C; 1 hr., 17000 lbs. pressure	0.002	9.1	10.6	7
Heated at 560 C; 2 hr.	0.002	7.40	4.07	8
Heated at 560 C; 14 hrs.	0.005	7.43	11.9	11
.. .. ..	0.003	6.19	27.87	12
Heated at 560 C; 14 hrs.	0.005	33.15	63.8	13
.. .. ..	0.005	4.76	5.78	14
.. .. ..	0.0035	5.25	2.03	17
.. .. ..	0.003	7.47	1.3	19

Subsequent Treatment	Thickness (inches)	Dielectric Constant	Power Factor	Number
Heated at 560 for 14 hrs.	0.003	9.64	57.9 (percent)	20
Heated at 184 C; 1 hr., 17000 lbs. pressure	0.00175	7.01	2.3	21
.. .. ..	0.0015	8.44	11.9	22
.. .. ..	0.00175	9.92	68.6	23
Heated at 560 C for 14 hrs.	0.002	6.41	12.5	101
.. .. ..	0.0035	11.96	46.8	102
.. .. ..	0.010	20.6	----	103
.. .. ..	0.0015	8.38	83.5	104
.. .. ..	0.0045	5.34	7.58	106
none	0.015	5.30	17.1	112

TABLE VII (Continued)

Sample Number	Clay Used	Remarks on Film Preparation	Base Exchange Agent
20	Wyodak micro-mesh	Clay suspension poured to 2 mm. thickness, then dried at 50 C in cabinet	Saturated mercuric nitrate solution
21	..	.. ..	Saturated lead acetate solution
22	..	.. ..	Saturated mercurous nitrate solution
23	..	.. ..	Saturated mercuric nitrate solution
101	..	Film formed from colloidal gel of clay containing a 1.2 percent soln. of $BaCl_2$	none
102	..	Film formed from colloidal gel of electrodialyzed clay	..
103	..	Same as 101 except that a 10 percent soln. of $BaCl_2$ was used.	..
104	American Colloid Volclay	This film formed by air drying at R. T. for 48 hrs.	..
105	..	Same as 104 but dried in oven at 50 C.	..
112	Fisher Bentonite		..

Subsequent Treatment	Thickness (inches)	Dielectric Constant	Power Factor	Number
Heated at 560 C for 14 hours	0.0025	3.93	34.36	201
.. ..	0.004	9.85	29.6	301
.. ..	0.0035	7.64	2.8	302
.. ..	0.006	5.31	5.4	303
.. ..	0.004	4.99	9.15	304
.. ..	0.003	3.12	5.4	307
.. ..	0.0015	1.29	81.4	308
.. ..	0.002	1.59	57.4	310

TABLE VII (Concluded)

Sample Number	Clay Used	Remarks on Film Preparation	Base Exchange Agent
201	Wyodak micro-mesh	Clay suspension poured to 2 mm. thickness, then dried at 50 C. in a cabinet	Saturated cerium nitrate solution
301	..	.. ..	Saturated sodium stannate solution
302	..	.. ..	Saturated $CoCl_2$ solution
303	..	.. ..	Saturated cadmium acetate solution
304	..	.. ..	Saturated $Cr_2(SO_4)_3$ solution
307	..	.. ..	Saturated $Th(NO_3)_4$ solution
308	..	.. ..	Saturated aluminum potassium sulfate solution
310	..	.. ..	Saturated uranium acetate solution

of one hour and then a continued heating at this temperature for a period of 14 additional hours. The film strips, cut three inches by two inches, were placed between glass plates to keep them from curling. A Lindberg furnace was employed. It appeared to be critical that the initial rise in temperature to 550 degrees Centigrade be not too rapid. With rapid increases in temperature the film would be reduced to dust as it was dehydrated. When the treatment was carried out in the regular way the films became black in color and were much more brittle than they were before the curing step.

TESTING OF THE FILM FOR DIELECTRIC CONSTANT AND POWER FACTOR

A GENERAL RADIO Type 716-C Capacitance Bridge with Type 1302-A Oscillator and Type 1231-B Amplifier and Null Detector was used in the testing procedure. A mercury electrode holder specially made according to a model submitted by Mr. F. H. Wells (16) was employed to hold the film strip. The electrode had a one square inch surface area contact between both sides of the film and the mercury which connected in turn with shielded leads to the bridge itself.

Before the test of a film, the film was kept in a drying oven at 100 degrees Centigrade for at least 24 hours. The test was made never more than 15 minutes after the strip was removed from the oven. The electrode holder was kept in a desiccator until the time of the test. Under such conditions, daily humidity fluctuations did not seem to be of much importance. A film which was tested two hours after removal from the oven would have increased noticeably in power factor.

The properties and average test results of the various films

prepared are given in Table VII.

RESULTS

An analysis of the data in Table VII indicates several interesting facts. Wyodak films seem to be superior to American Colloid films if the base exchange and subsequent treatment has been identical. Compare samples 1 and 8, 11 and 12 for values of the dielectric constant and the power factor. It is of interest to see the differences in chemical composition of these two clays. See Table II.

Samples 11 and 17 seemed to indicate that the use of the free base of the metal is to be preferred to the use of the saturated salt of the metal although the salt is definitely much more soluble in each case.

From samples 1 and 2 it appeared that longer periods of heating in the furnace greatly improved the power factor with only slight reduction in the dielectric constant.

In a few cases increase in molecular weight of the cation in the base exchange reaction seemed to cause the power factor of the film to decrease (samples 8, 11 and 19). In many other cases that relation did not hold true. A consistent but unexplained difference existed between the effect of mercurous and mercuric cations in the base exchange (samples 19, 20, 22, and 23).

Substitution of pressures up to 17000 lbs. per sq. in., shorter periods of heating and lower temperatures in place of the 560 degree Centigrade and 24 hour curing period did not give comparable results, as far as the power factor was concerned (contrast samples 19 and 22, 2 and 7). However, a one hour period at 175 degrees Centigrade and 17000 lbs. per sq. in. seemed to be more favorable than a ten minute treatment under the same conditions (see samples 5 and 7).

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